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14. ABSTRACT

Polymeric EO modulators operating with drive voltages of 0.8-4.5 volts, bandwidths of 150 MHz, and insertion losses on the order of 5-6 dB have been demonstrated. These modulators have also been packaged as 3-D circuit structures and integrated directly with VLSI semiconductor electronics and with silica fiber optics. A variety of new device structures including phased array radar, ultrafast analog-to-digital converters, polarization insensitive modulators, ultrahigh bandwidth oscillators, and spatial light modulators have been demonstrated. New condensed matter theory has been developed which is capable of correctly predicting for all concentration regimes the behavior of many-body, spatially-anisotropic, long-range electrostatically-interacting dipolar molecules. This theory has guided the dramatic improvement in organic EO materials.

15. SUBJECT TERMS

Electro-optic materials, electric field poling, reactive ion etching, high bandwidth modulators, materials integration, high hyperpolarizability

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**SYNTHESIS AND PROCESSING OF IMPROVED SECOND
ORDER NONLINEAR OPTICAL MATERIALS
F49620-97-1-0307**

FINAL TECHNICAL REPORT

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REVIEW OF OBJECTIVES

The objective of this research is to define and implement structure/function relationships relevant to the optimization of second order nonlinear optical activity. This includes optimization of the molecular hyperpolarizability of second order chromophores and optimization of electrical field induced electro-optic activity. Structure function relationships will be defined by a combination of theoretical calculations and the systematic investigation of material electro-optic activity as a function of chromophore loading in various polymer matrices. Issues of the processing of second order nonlinear optical materials will also be addressed with particular attention given to defining processing conditions leading to maximum electro-optic activity, minimum optical loss, and maximum stability of second order nonlinear optical activity.

STATUS OF EFFORT

During the contract period, we have made dramatic progress and have demonstrated polymeric EO modulators operating with drive voltages of 0.8-4.5 volts, bandwidths of 150 GHz, insertion loss of 5-6 dB, and packaged into 3-D integrated systems. Our advances have been based on the definition of critical structure/function relationships and upon developing new materials synthesis and processing procedures. Explicitly, we have, during the contract period, developed new equilibrium and molecular dynamics statistical mechanical treatments for the interaction of many particles characterized by large dipole moments and molecular polarizabilities. These theoretical advances have permitted us to quantitatively predict the variation of electro-optic activity of electrically poled materials as a function of chromophore loading in a polymer matrix. Not only does our theoretical treatment correctly predict the maximum observed in a plot of EO activity versus chromophore concentration, but our theory also predicts the dependence of EO activity upon chromophore shape. With guidance from theory, we have systematically modified chromophores and dramatically improved macroscopic electro-optic activity. Indeed, our advances have led to the demonstration, by ourselves and by companies such as TACAN Corporation, of polymeric EO modulators operating with drive voltages as low as 0.8 volts (the lowest value achieved for any material). Our theoretically defined structure/function relationships suggest that dendritic structures are particularly attractive not only for improving maximum achievable electro-optic activity but also for reducing optical loss, improving processability, and material stability under harsh operating conditions.

State-of-the-art electro-optic materials have been provided to a number of companies and government laboratories in support of prototype device development efforts.

II. PROGRESS REPORT (F49620-97-1-0307)

A. Polymeric Electro-Optic Materials

For an electro-optic (EO) material to be useable for device fabrication, a number of criteria must be satisfied simultaneously, including large EO activity, low optical loss, exceptional stability (including thermal, chemical, electrochemical, and photochemical), and good processability. To simultaneously satisfy all of these requirements in a single material requires solving many of the most difficult problems of material science including that of efficiently fabricating acentrally-ordered molecular lattices that are both processable and robust. It has only been during the past year that polymeric materials have been able to match and/or exceed the performance of inorganic materials (lithium niobate and gallium arsenide) in all categories mentioned above. Fortunately, considerable room for further improvement exists for organic materials and these improvements should dramatically increase the utilization of polymeric EO materials for applications ranging from telecommunications, to optical gyroscopes, to phased array radar. In the following paragraphs, we provide an overview of major advances in polymeric EO materials achieved with AFOSR support. Details of these achievements can be found in the 81 publications derivative from the past two and a half years of research.¹⁻⁸¹ Our discussion below is focused on the production, by the process of electric field poling, of polymeric EO materials containing covalently-coupled chromophores. Many of our observations, including the importance of considering intermolecular electrostatic interactions, are relevant to other methods of producing EO materials, including by sequential synthesis and crystal growth self-assembly methods. For the most part, our research has focused on developing EO materials for application at the telecommunication wavelengths of 1.3 and 1.55 microns.

1. Chromophore Design: A New Paradigm

The most dramatic structure/function relationship elucidated during the past three years has been the role played by intermolecular electrostatic interactions in defining maximum realizable electro-optic

activity. Before our work, molecules exhibiting large first hyperpolarizability (molecular second order optical nonlinearity) were assumed to behave as independent particles under the influence of an electric poling field. Thus, macroscopic EO activity was predicted to exhibit a linear dependence on chromophore loading (number density) in a polymeric matrix and the figure-of-merit for comparing chromophores was taken to be $\mu\beta/\text{MW}$, where μ is the chromophore dipole moment, β is the chromophore first hyperpolarizability, and MW is the chromophore molecular weight. Thus, a chromophore such as the Sandoz chromophore (prepared by Sandoz Corporation and explored by numerous researchers including those at Akzo Nobel) was predicted to lead to an EO material 14 times more active than the well known Disperse Red chromophore [see Table 2, reference 27 for the structures and relevant optical properties of these chromophores]. In reality, the best EO activity (and a transient activity at that, since the Sandoz chromophore is unstable under electric field poling conditions) that could be obtained in practice was 3 to 4 times that obtained for Disperse Red. This dramatic difficulty encountered in the attempted translation of large microscopic (molecular) optical nonlinearity to macroscopic optical nonlinearity made the intelligent design of chromophores impossible until the basis of the problem could be elucidated. During the period of AFOSR contract F49620-97-1-0307, we undertook a systematic theoretical and experimental investigation of the problem of translating molecular optical nonlinearity to macroscopic electro-optic activity. Experimentally, we observed, for all chromophores with dipole moments and molecular polarizabilities exceeding those of Disperse Red, a maximum in the plot of material EO coefficient versus chromophore loading (number density) in the polymer matrix. With increasing chromophore dipole moment and polarizability, the position of these maximums shifted to lower values of number density. Also, the position of the maximum was subsequently observed to depend on chromophore shape.

In an effort to quantitatively understand experimental results, we undertook the explicit theoretical treatment of intermolecular electrostatic interactions among chromophores, as such interactions were a logical cause for the observed concentration-dependent phenomena. We, of course, as discussed at length in reference 27 systematically ruled out other possibilities such as electric conductivity associated with ionic impurities. The theoretical treatment of many body interactions is by no means trivial. While treatment of intermolecular electrostatic interactions employing a variety of potential functions has been attempted since the time of London,^{3,82} the focus has largely been upon intermolecular association (condensation and phase transition phenomena) rather than upon molecular order. Virtually, all potential functions used in calculations before our work were isotropic in nature, such as the London 6-12 potentials (where the orientation dependence between pairwise interacting particles have been averaged out). We were immediately faced with two formidable theoretical problems. The first is the obvious need to explicitly treat the spatially anisotropic electrostatic interactions existing among chromophores (If a chromophore has a dipole moment, it is obvious that the intermolecular electrostatic interactions will be anisotropic in nature). The second issue to be faced is that (with large dipole moments and polarizabilities) intermolecular interactions are sufficiently long range that a pairwise treatment of interacting particles is no longer a reasonable approximation. Thus, we were faced with the full complexity of the many body problem and treatment of up to 50 simultaneously interacting particles had to be considered. This assumed, of course, that the problem could be handled within the framework of equilibrium statistical mechanics, i.e., that the competition of chromophore-poling field and chromophore-chromophore intermolecular electrostatic interactions could be described by an "effective field" approach, where the interactions add vectorially at a given chromophore. Suppose intermolecular electrostatic interactions drive chromophore aggregation and phase separation? Such phenomena could be simulated only by a molecular dynamical computational approach where diffusional effects are explicitly considered. Fortunately, as described in our recent publications, dramatic progress has been made on both equilibrium and non-equilibrium statistical mechanical computational approaches.^{3,8,21,27,40,47,55,56,78} Indeed, it can be stated that the agreement between theory and experiment appears nearly quantitative. Even more exciting, the theoretical approaches developed in our work should clarify a number of previously unexplained phenomena in materials science (as will be discussed later in this proposal).

Let us first discuss our equilibrium statistical mechanical treatment of the problem of the competition of poling field and intermolecular interactions. Experimental light scattering studies (as a function of chromophore loading in various polymer matrices) suggested that non-transient aggregation was not a serious problem. This result provided support for the reasonableness of an equilibrium statistical mechanical approach. In such a treatment, one attempts to calculate an equilibrium expectation value of an observable such as an electro-optic coefficient or equivalently the acentric order parameter $\langle \cos^3 \theta \rangle$ associated with that observable. As discussed at some length in references 56 and 78, computational problems include developing approximations for the many body nature of the problem and for the large number of integrations that must be performed with respect to the orientational variables relating chromophores to each other and to the electric poling field (the laboratory axis system). We have followed an effective field approach whereby we compute the resultant field felt by a reference chromophore in the presence of the poling field and fields from a collection of say 50 or so surrounding chromophores. Integration over orientational variables is dramatically simplified by positioning chromophores interacting with the reference chromophore along a "director axis" (see Fig. 1). The effective field produced by chromophores for a given orientation

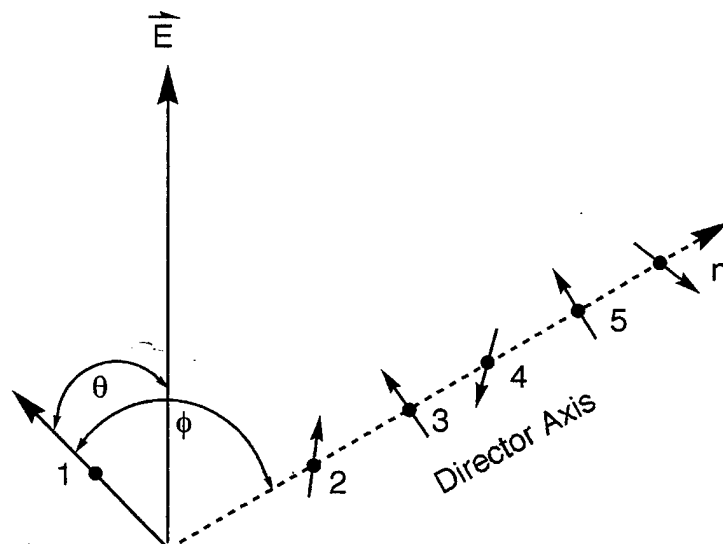


Fig. 1. Coordinate systems relevant to the equilibrium statistical mechanical treatment of the competition of poling field and intermolecular electrostatic interactions. Angles θ and ϕ (appropriate for the most approximate treatment—spherical chromophores and averaging over the orientations of chromophores 2...n with respect to the director axis) are more correctly Euler rotation matrices.

of the director axis with respect to the axis system of the reference chromophore is computed by averaging over all the relative orientations of the chromophores (other than the reference chromophore) positioned along the director. Our approach is conceptually similar to an approximate (effective field) treatment of multiple particle intermolecular electrostatic interactions developed by Piekara.⁸³ This simplifies (by making use of well-known trigonometric relationships) to integrating over two rotation matrices; namely, the matrix relating the director axis to the axis system of the reference chromophore and the rotation matrix relating the reference chromophore axis system to the laboratory axis system. In the simplest incarnation, the problem reduces to integrating over just two angles (although many integrals must still be computed). For spherically symmetrical chromophores in the most simple formulation of the problem, an analytical result can be obtained (which is quite amazing given the number of integrals that must be evaluated⁵⁶). The analytical result has a wonderfully straightforward physical interpretation; namely, that intermolecular electrostatic interactions among chromophores act to attenuate poling-induced macroscopic EO activity. The attenuation factor is simply $[1 - \bar{L}^2(W/kT)]$ where L is the Langevin function, W is the orientationally-averaged 6-12 potential first calculated by Frank London,⁸² k is the Boltzmann constant, and T is the Kelvin temperature. The dependent variable, W/kT , is simply the ratio of intermolecular electrostatic interaction energy W (the sum of dipole-dipole, induced dipole, and dispersion energies) to thermal energy kT . Since W depends quadratically on chromophore number density (concentration), this analytical result correctly predicts electro-optic

activity should decrease at high chromophore loading, i.e., the quadratic dependence in the attenuation factor overwhelms the linear dependence (which dominates at low loading). The simple analytical result also correctly predicts, qualitatively, the observation that the position of the maximum in a plot of EO coefficient (r) versus number density (N) shifts to lower N with increasing chromophore dipole moment and polarizability (i.e., increasing W). The simple analytical result identifies the general nature of the problem but provides no insight as to how we can minimize the problem by molecular design. A more useful equilibrium statistical mechanical calculation is one that explicitly considers chromophore shape and the influence of molecular shape on maximum realizable electro-optic activity. Such consideration forces use of numerical methods. A representative set of numerical results, shown in the accompanying Fig. 2, illustrates the salient features of our numerical theoretical calculations. Our equilibrium statistical mechanical numerical results illustrate that the maximum in the plot of macroscopic EO activity versus chromophore number density shifts to lower loading with changing chromophore shape from spherical to prolate ellipsoidal. This is completely reasonable when it is realized that approach of two chromophore along the direction of their dipole moments actually favors acentric ordering of chromophores, while side by side approach strongly favors centric ordering. Of course, the strength of intermolecular electrostatic interactions increases dramatically with decreasing separation, so the close side-by-side approach afforded by a prolate ellipsoidal structure is particularly problematic for attenuating poling-induced EO activity. **Numerical calculations (explicitly treating chromophore shape) suggest a simple paradigm for improving the electro-optic activity that is realized with a particular π -electron core structure.** Namely, if a second-order nonlinear optical chromophore is derivatized with bulky (but electroactively inert) substituents that make the chromophore appear more spherical, then electro-optic activity should increase. We have carried out a variety of derivatizations of various chromophore structures and in all cases we have observed increases in electro-optic activity. A particularly intriguing and recently explored derivatization approach is a dendritic synthesis scheme (see Fig. 3).

With such an approach to systematic chromophore modification, we have observed an increase in the electro-optic activity of the FTC chromophore to near the theoretically-predicted optimum value of 100 pm/V. Structural modification of chromophores has not only improved maximum achievable electro-optic activity for a given chromophore type but has also resulted in reduction in optical loss and improvement in solubility. Improvement in chromophore solubility has, in turn, dramatically improved processibility. In some cases, structural modification has led to improvement in chromophore stability.

Agreement between theory and experiment is a necessary but not sufficient condition for the validity of a given theoretical approach. A point of continuing concern is the appropriateness of the approximations used in the equilibrium statistical mechanical approach. Recently, we have succeeded in implementing a theoretical approach to the problem from a molecular dynamical perspective but employing realistic, spatially-anisotropic intermolecular potential functions. In our molecular dynamical calculations, the evolution of a lattice of up to 1000 interacting chromophores (in a polymer

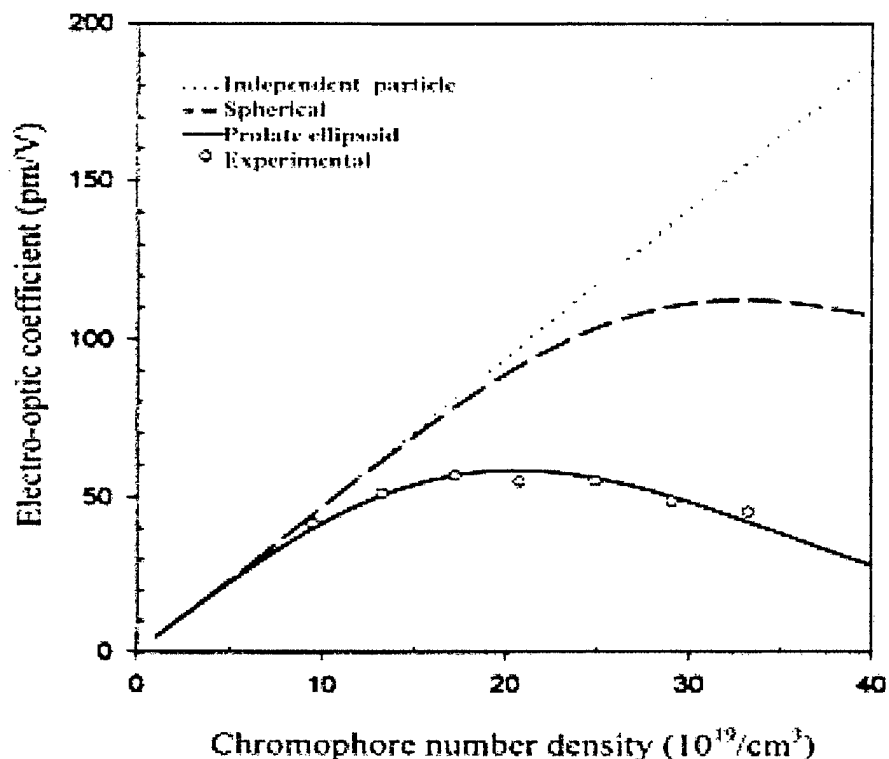


Fig. 2. Experimental and theoretically-predicted variation of electro-optic coefficient with chromophore number density (concentration) is shown for the FTC chromophore in a PMMA matrix.⁴⁷

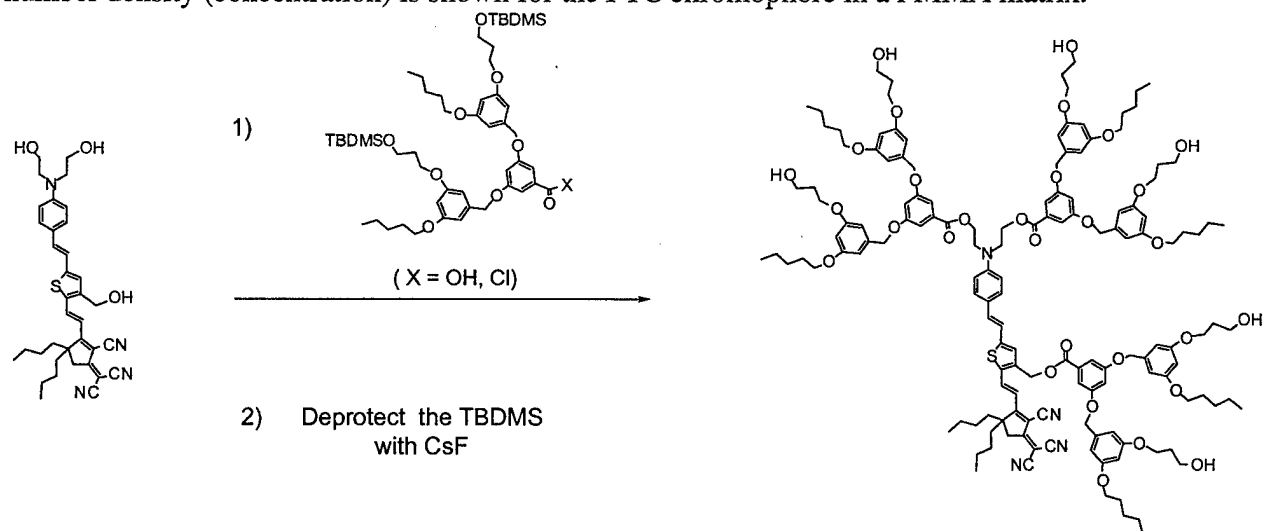


Fig. 3. Systematic modification of the FTC chromophore to a G-2 dendrimer structure is shown.

matrix) is followed. A molecular dynamical approach has the advantage of permitting examination of the details of the distribution of particles and not just a single order parameter. Moreover, various interactions such as the externally applied electric poling field and various intermolecular electrostatic interactions can be turned on and off. The time dependence of the evolution of particles can be followed as well as examination of equilibrium distributions. Representative results are shown in Figs. 4 and 5. In Fig. 4, we show the temporal evolution (more correctly, the evolution with number of computational steps where the energy minimization criteria of standard molecular dynamical calculations are satisfied in each step) of order parameters, $\langle \cos^n \theta \rangle$, from $n = 1$ to $n = 4$. Note that EO activity is associated with the $n = 3$ parameter while birefringence and dipole moment are associated

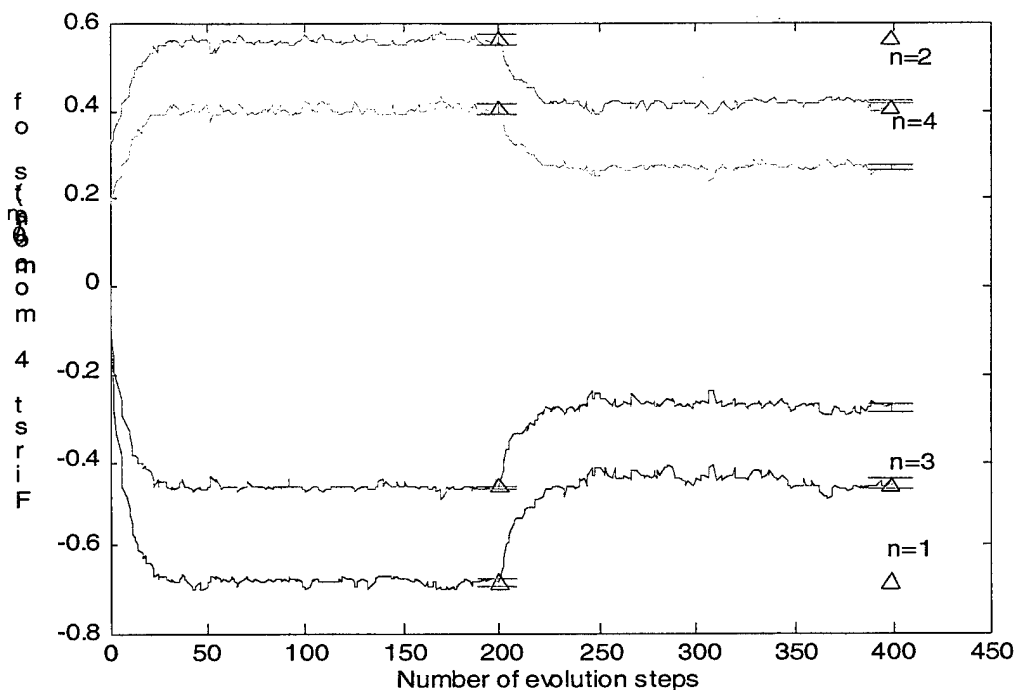


Fig. 4. The calculation of the first four order parameters ($n = 1$, blue; $n = 2$, green; $n = 3$, red; $n = 4$ aquamarine) by a molecular dynamics scheme explicitly treating the spatial anisotropy and many body nature of the intermolecular interactions is shown. The calculation is for a 1000 chromophore lattice. Initially, chromophores experience no poling field or intermolecular interactions; thus, the chromophores are randomly oriented and $\langle \cos^1 \theta \rangle = \langle \cos^3 \theta \rangle = 0$. A constant poling field is turned on at step 1 (but no intermolecular interactions exist); the order parameters rapidly evolve to values predicted by equilibrium statistical mechanics (red bars). At step 200, intermolecular electrostatic interactions are turned on. Note the attenuation of order parameters produced by intermolecular electrostatic interactions competing with the poling field. The molecular dynamics result rapidly converge to the results from equilibrium statistical mechanics (red bars). Please forgive the distortions that appear in this and other figures as the result of cutting and pasting from the original program output into this word document. The y-axis label should read "First 4 moments of $\langle \cos^n \theta \rangle$ ".

with $\langle \cos^1 \theta \rangle$. Initially, the poling field is turned off and as expected the $n = 1$ and $n = 3$ order parameters are zero. The poling field is then turned on but intermolecular interactions are left off. The numerical results quickly (in less than 50 lattice evolution steps) converge to the well known equilibrium statistical mechanical results (indicated by red bars), e.g., $\langle \cos^3 \theta \rangle = \mu E / 5kT$. At step 200, intermolecular electrostatic interactions (which extend over about 30-50 particles) are turned on. Note the attenuation in the $n = 1$ and $n = 3$ order parameters as the result of intermolecular electrostatic interactions. For the particular magnitudes of chromophore dipole moment and polarizability used in the calculations shown in Fig. 4, the molecular dynamical calculations rapidly evolve to the values obtained with our equilibrium statistical mechanical numerical methods. Fig. 5 also supports the validity of use of an effective field equilibrium statistical mechanical treatment. The distribution of chromophores suggests that the most probable chromophore orientation points along the resultant of the vectorial addition of the applied poling field and the fields from surrounding chromophores. The molecular dynamical calculations should be applicable to a wide range of chromophores and poling conditions and should provide even more detailed insight into pathways to optimize macroscopic EO activity, including the influence of chromophore size and shape upon the dynamics of reorientation of chromophores under applied fields.

Our theoretical calculations have added an important new dimension to the design of chromophores and are responsible for the development of materials that for the first time exceed the

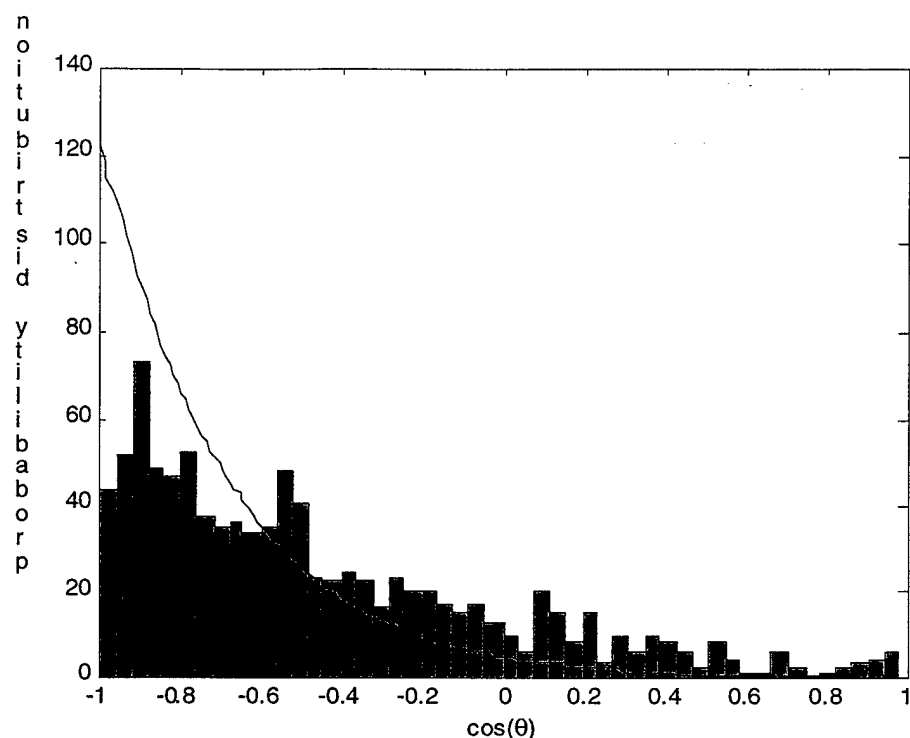


Fig. 5. The probability distribution of chromophore orientations for the case of independent particles (black line) and the case of full electrostatic interactions (bar graph). The former corresponds to step 200 of Fig. 4 while the latter corresponds to step 400 of Fig. 4.

electro-optic activity of lithium niobate. Using EO materials produced in our laboratory, companies such as TACAN have fabricated electro-optic modulators with drive voltage (V_π) requirements of less than one volt (at 1.3 microns wavelength)—see Fig. 6. Working with Professors Steier (USC EE) and

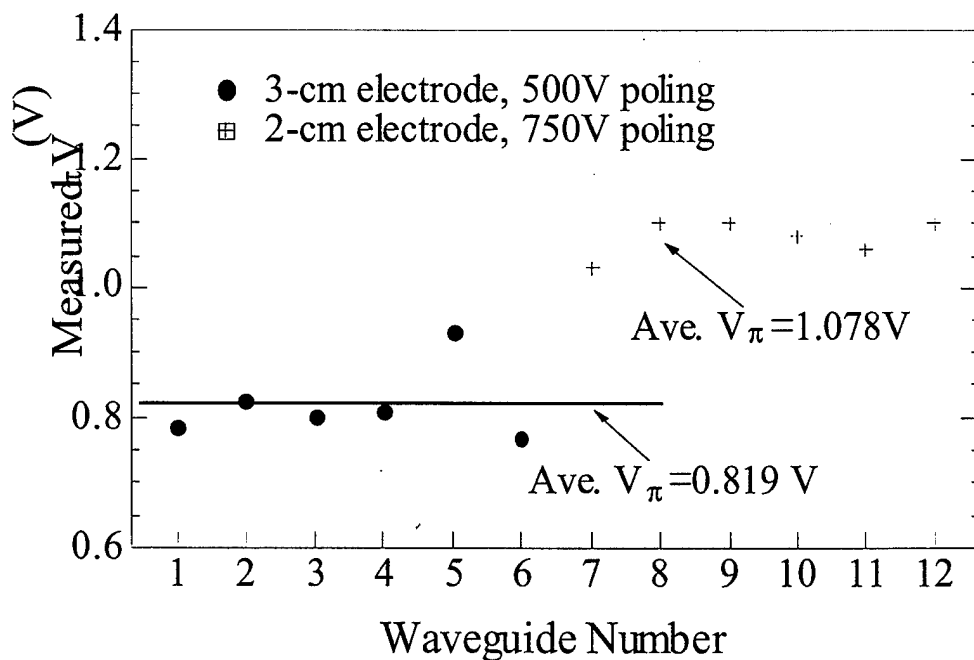


Fig. 6. Measured V_π values (at 1.3 μm) are shown for six 3 cm and six 2 cm pathlength Mach Zehnder modulators fabricate by TACAN Corporation of Carlsbad, CA using our CLD chromophore/polymer materials. No significant change in V_π values were observed over a 1000 hours.

Fetterman (UCLA EE), we have fabricated modulator devices that operate at voltages of 1 volt or less. We hasten to add the following comment to the preceding statement. While realization of halfwave voltages of 1 volt is a critically important advance, even lower voltages are required for a number of applications in information processing and RF distribution. Moreover, a 1 volt V_π must also be accompanied by low optical loss, exceptional material stability, and excellent processability with each application characterized by its unique requirements. In short, our work has just begun, particularly given that polymeric EO materials must compete with and displace commercially established lithium niobate and gallium arsenide materials (although some would argue that gallium arsenide multiple quantum well (MQW) electro-absorptive materials are still essentially in development).

In addition to designing chromophores for improvement in macroscopic electro-optic activity, we have also succeeded in effecting dramatic improvements in chromophore stability. A number of chromophores with thermal stabilities in the range 275 to 425°C have been synthesized while at the same time retaining high optical nonlinearity (values of $\mu\beta$ in excess of $10,000 \times 10^{-48}$ esu (at 1.9 microns wavelength)). While we have systematically explored a number of donors, acceptors, and π -electron bridge structures (and opportunity for further improvement clearly exists), a particularly important advance achieved in our laboratory was realization of the suitability of tricyanofuran acceptor groups. Unlike Sandoz and thiobarbituric acid acceptors, this acceptor group is extremely robust leading to materials that are well suited for device fabrication. Chromophore/polymer materials exploiting this acceptor (which we designate FTC, CLD, and GLD for variants with different π electron bridge structures) are now being explored in devices by a number of companies (Lockheed-Martin, Pacific Wave Industries, TACAN, Allied Signal, Radiant Research, etc.) and Federal laboratories (China Lake Naval Weapons Laboratory, the Air Force Wright Laboratories).

In addition to EO activity and stability, two other performance criteria must be kept in mind when designing chromophores. These are optical loss (from both absorption and scattering) and lattice hardness (used to lock-in poling-induced electro-optic activity). Since these issues involve polymer as well as chromophore design we deal with them in the following section on polymer design.

2. Polymer Design: Optical Loss and Lattice Hardness Issues

The issue of stabilizing poling-induced electro-optic activity by design and fabrication of hardened polymer lattices appears deceptively simple. By control of the stiffness of polymer segments and the number of crosslinks connecting polymer chains virtually any degree of lattice hardness can be obtained. The trick is to obtain a desired degree of lattice hardness (hence thermal and photochemical stability of electro-optic activity) without trading-off EO activity, optical loss performance, and processability to unacceptable degrees. For example, chromophore/high glass transition polymer (e.g., polyimide) composites can lead to EO materials characterized by exceptional thermal stability. However, the poor solubility of these materials in traditional spin casting solvents and the requirement of high poling temperatures has, in general, led to unacceptably low optical nonlinearity and unacceptably high optical loss. Photo-initiated crosslinking (hardening) reactions have not worked for polymeric EO materials because of competition of the EO chromophore with the photo-initiator for absorption of light.

We have attempted to obtain optimized materials by introduction of specific chemical modifications at various stages (e.g., lattice hardening by crosslinking subsequent to the induction of acentric order by poling) where those modifications are most appropriate. Not only have a number of lattice hardening chemical reactions been explored (including a variety of thermosetting methods) but we have investigated in detail the dependence of properties such as the magnitude and stability of electro-optic activity and the magnitude of optical loss on conditions such as reaction stoichiometry, etc. With careful elucidation of structure/function relationships, significant improvements have been achieved as discussed in detail in references 25,27,31,47,56,56,60-63,65,75. In particular, poling-induced optical loss has been reduced to insignificant values with appropriate attention to details such as the temporal control of lattice hardness, which in turn depends upon control of both temperature gradients and reaction stoichiometry.

Until the past grant period, our research focused on developing EO materials for application at the telecommunication wavelength of 1.3 microns. At this wavelength, optical loss from either interband electron absorption or absorptions associated with C-H (also O-H and N-H) vibrational overtones are relatively unimportant. Experimentally-observed optical loss is typically dominated by scattering loss due to either material heterogeneity (including that introduced by processing) or material damage (e.g., surface damage occurring during electric field poling or deposition of cladding

layers). With attention to processing conditions, materials exhibiting optical loss values in the range 0.7-1.0 dB/cm (at 1.3 μm) can be systematically produced. Recently, in response to interest at Lockheed-Martin, PWI, Allied Signal, DoD laboratories, etc., we have undertaken development of materials for applications at 1.55 micron telecommunications wavelength. At this wavelength, absorption associated with C-H vibrational (also O-H and N-H vibrations for thermosetting materials) overtones, contribute significantly to optical loss. Without partial isotopic replacement of protons it is difficult to achieve optical loss values less than 1.5 dB/cm. With partial halogenation, we have shown that it is possible to achieve optical loss values comparable to those obtained at 1.3 microns wavelength.⁸⁴ For device applications at 155 microns, optical loss associated with O-H and N-H vibrational overtones are particularly problematic because of the ease of proton exchange. This problem has motivated us to seek alternatives to traditional thermosetting urethane and epoxidation lattice hardening reactions. More will be said concerning this issue in the proposed research section. Modification of chromophores and polymers by partial halogenation has on occasion produced significant changes in solubility which, in turn, have required re-definition of spin casting conditions.

3. Materials Processing: Optimizing a Multi-Variable Protocol

The performance characteristics (electro-optic coefficient, optical loss, etc.) of a hardened electro-optic material can depend on a large number of conditions including solubility of materials in spin casting solvents, the dielectric breakdown of intrinsic and partially hardened materials (hence, electric field strength), the temperatures at which poling and hardening are effected, etc. For example, for thermosetting materials, stepped electric field and temperature poling protocols has been found to be found to lead to the largest EO activity and the best thermal stability of that activity. Avoidance of exposure to atmospheric moisture can be important for certain thermosetting reaction schemes. Lattice hardness (hence, control of processing conditions) can dramatically influence the level of optical loss associated with deposition of cladding layers. The hardening of cladding layers by UV curing can significantly effect the performance of polymeric EO waveguide circuits.

Production of buried channel EO waveguides by techniques such as reactive ion etching (RIE) and electron cyclotron resonance etching (ECRI) is influenced by lattice hardness and by the kinetic energy of reactive ions. With appropriate control of starting materials and processing conditions, optical loss associated with the production of buried channel waveguides can be reduced to insignificant values (0.01 dB/cm). As might be expected, optimum processing conditions vary with each new polymeric material.

4. New Insights

Given the multi-variable dependence of materials processing, the question arises: "Is there an approach that permits systematic variation of given molecular components of a polymeric EO material without redefining all processing conditions?" A new insight realized during the past several months is that dendrimer structures may be ideally suited not only for optimizing electro-optic activity but also for simplifying the complexities of material processing. As predicted by molecular dynamical statistical mechanical calculations, the solubility of EO chromophore-containing dendrimer structures increases through G-2 dendrimers. Dendrimer molecular structures can be modified to improve optical transparency at 1.55 microns without dramatically modifying solubility in spin casting solvents. Moreover, dendrimer structures appear to provide steric protection of chromophores so that chromophores appear to be more robust under a wider variety of processing conditions. Finally, lattice hardening appears to be capable of being effected with less attenuation of poling-induced EO activity. Dendrimer structures thus appear to be an exciting new avenue to pursue to systematically develop general processing protocols. Of course, work of dendrimer structures is new and the general validity of our preliminary observations need to be verified for several chromophore systems.

5. Photoprocessing: Trimming & Actuation

a. Trimming

We have introduced a new photolithographic technique that we refer to as multi-color photolithography which simply makes use of the fact that the penetration depth of light for a given material system is wavelength dependent. By controlling the wavelength and exposure time of light effecting a photochemical or photophysical change, sophisticated three dimensional optical circuits can be fabricated and the performance of integrated optical circuits can be fine tuned. Multi-color photolithography is a completely dry process and frequently involves half the number of step of circuit production by reactive ion etching. We have also shown that optical (or photochemical) poling can be used to enhance the efficiency of electric field poling. This technique, initially introduced by the

Dalton group in the late 1980s, continues to receive considerable international attention.

The details of optical (photochemical) trimming of circuit performance and fabrication of optical devices by photo-processing are provided in references 10,12,24,27,44,47,55,85.

b. Opto-mechanical actuation

In 1991 while studying azobenzene chromophores covalently coupled to main chain polymers, we observed that irradiation with both polarized and unpolarized visible and UV light produced large changes in index of refraction (changes as large as 0.4 were observed) and birefringence.⁸⁶ These changes can be associated with photo-initiated trans-cis-trans isomerization of the azobenzene chromophores. Since the absorption cross-section reflects the symmetry of the π -electron structure, irradiation with polarized light drives chromophores to molecular orientations with respect to the irradiating light where the chromophore can no longer absorb light. This is the physical basis of the observed birefringence. If irradiation is through a grating mask, azobenzene chromophores absorbing light will "swim" (by photo-initiated trans-cis-trans conformational changes) to dark regions of the material. Because the chromophores are coupled to polymers they pull the polymer along and relaxation of the structure (when the light is turned off) is delayed by polymer dynamics. The material density changes associated with translational movement of chromophores are responsible for the large index of refraction changes. Examination of such azobenzene materials with STM/AFM techniques reveals a ribbed structure. Thus, the swimming motion of azobenzene chromophores has caused translational displacements of exposed regions of the material and provides a mechanism of opto-mechanical actuation. This actuation is reversible by changing exposure conditions.

With Hughes Research Laboratories, we are exploring commercial applications of this phenomena.

6. 3-D Integrated Circuits Through Novel Mask Lithography

A major achievement of our previous research is pioneering the integration of polymeric electro-optic circuitry with silica fibers and with VLSI semiconductor electronic circuitry (references 1,9,11,14,16,17,26,27,35,40,42,51,53,55,57,60,64,70,75). Each integration poses unique difficulties. Silica fibers (fabricated for low loss transmission of 1.3 micron light) have core dimensions of 0.8-1.0 microns (spherical mode) while polymeric EO waveguides have core dimensions of approximately 5x2 microns (elliptical mode). Thus, substantial mode mismatch exists if these two waveguide structures are simply butted together. Indeed, such coupling involves insertion loss of greater than 5 dB per connection--values that are unacceptably high. We have shown that coupling losses can be dramatically reduced by the fabrication of tapered transitions.^{9,14}

We have also shown high density vertical and horizontal integration of polymeric EO modulator circuitry with VLSI semiconductor electronics can be accomplished. Vertical integration involved overcoming the irregular surface topology of semiconductor wafers and fabricating deep vias (connection channels) for interconnecting EO drive electrodes to VLSI circuitry. Substantial advances in deposition and reactive ion processing has been achieved permitting fabrication of sophisticated "opto-chips" without degradation of the performance of either polymer EO or semiconductor electronic materials and circuits.^{1,11,26,40,47,55,57,63,75}

The most exciting advance in the past year has been the development of 3-Dimensional active/passive optical circuits through design and implementation of new materials processing techniques.^{35,42,51,53,55,57,60,63,64,75} In particular, we have found that use of Shadow, Gray-Scale, and Off-Set Photolithographic Masks permits development of low loss vertical waveguide transitions as indicated in the accompanying figure (Fig. 7).⁵³ Vertical transitions permits 3-D circuits to be fabricated and permits the development of unique EO modulators structures such as shown in Fig. 8.⁵³

The device structure shown in Fig. 8 permits light to be efficiently coupled (i.e., transitioned) from low loss passive polymeric waveguide (which does not contain EO chromophores and hence can be readily mode matched to silica fiber waveguide dimensions and can be fabricated from polymer structures leading to the lowest possible optical loss) to active EO polymeric waveguide (for signal processing) and back to passive waveguide. Such devices structures lead to insertion losses (4-6 dB total insertion loss depending on device length and less than 1 dB loss per connection) that are competitive with coupling lithium niobate modulators to silica transmission fibers. Insertion loss associated with gallium arsenide electro-absorptive modulators is currently much higher.⁷⁵

Development of techniques for producing 3-D optical circuits have proven critical for the production of special devices such a voltage controlled radiofrequency phase-shifters⁷⁰ (the key component of phased-array radar systmes) and optical network switches.⁷⁵

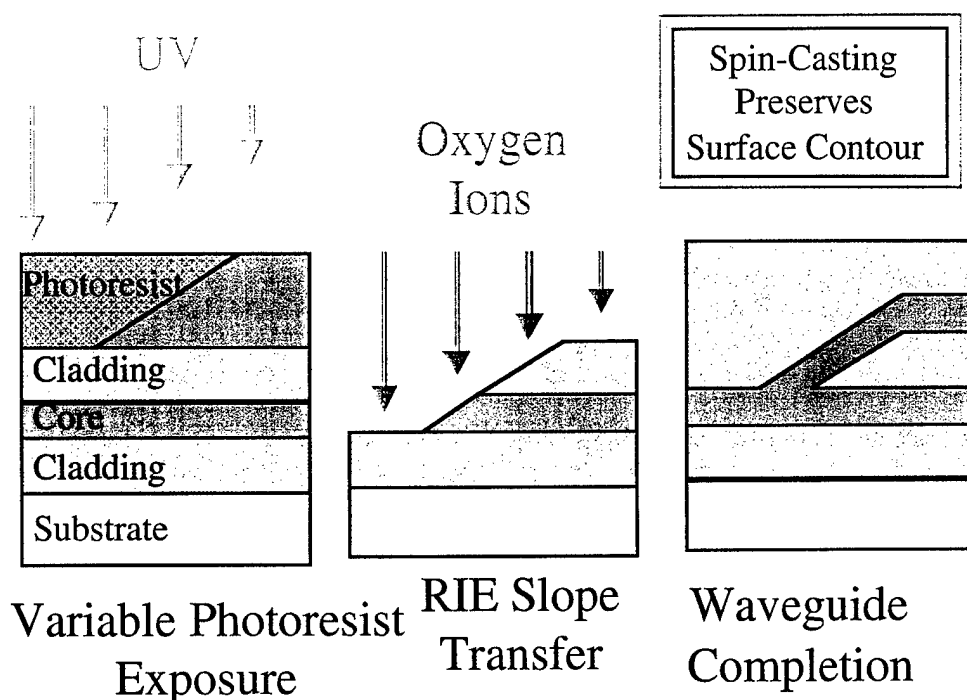


Fig. 7. The essential processing scheme for achieving vertical integration is shown. The initial sloped surface was fabricated employing shadow, gray scale, or off-set mask lithography.

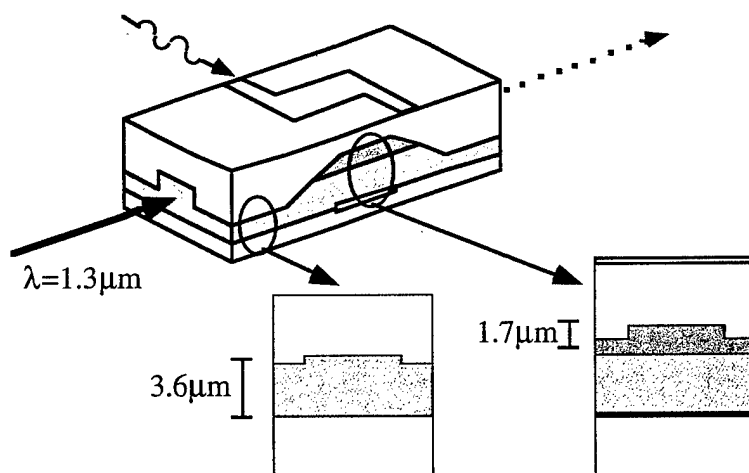


Fig. 8. A low loss polymeric electro-optic modulator is shown. The dark gray region is the active EO polymer waveguide while the light gray region is passive ultra-low loss passive polymer waveguide.

B. Dendrimers for Optical Amplification and Light Harvesting

1. Electronic Isolation

We have already shown that dendrimer structures can be used to attenuate unwanted intermolecular electrostatic interactions producing improved electro-optic materials. A collaboration with Professor Garito (Univ. of Penn.)⁷ motivated us to prepare a variety of dendrimer structures containing trivalent rare earth ion cores. Such structures dramatically attenuated self- and ligand-quenching of rare earth ion luminescence. Rare earth ion luminescence (e.g., Er^{3+} emission at 1.55 microns) was increased by more than two orders of magnitude relative to the luminescence observed for ions doped into high temperature processed silica. We also prepared rare earth core dendrimers with light harvesting

ligands positioned in various dendron generations. Among the criteria used was that the emission of an outer generation dendron overlap the absorption of the next inner generation dendron. Because dendrimer structures do not permit random orientation of light harvesting ligands relative to each other, light harvesting can be more efficient than predicted by Forster⁸⁷ theory. Energy transfer is readily calculated by our theoretical methods that can explicitly consider anisotropic intermolecular electronic interactions. Dendrimer structures have been fabricated that permit nearly 100% efficiency in light harvesting.⁷¹

While our initial involvement in the synthesis of dendrimer structures was initially driven by collaborations with Garito and with Jean Frechet⁸⁸ at Berkeley, it is clear that the ability to develop sophisticated 3-D optical circuits suggests that polymeric dendrimer materials containing lumophores for optical amplification and lasing might be usefully combined with polymeric circuit elements containing electro-optic dendrimers. In short, optical loss associated with passive/active polymeric optical circuits could be overcome by incorporating polymeric amplifying segments. Such amplification may be particularly useful for high density fan-in/fan-out backplane interconnects for high speed computers.

2. Spatially-Directed Transport

We have already demonstrated by the production of light harvesting dendrimers containing rare earth ion cores that spatially-directed (e.g., from the periphery to the core of the dendrimer structure) energy transfer can be efficiently effected. Applications can be readily extended to development of light emitting, lasing, photovoltaic, and photoelectrochemical materials where either energy or charge transport is spatially controlled.⁷¹ As each element of a dendrimer structure can be systematically modified, material performance can be systematically fine tuned. Incorporation of two-photon dyes into dendrimer structures affords interesting possibilities for 3-D imaging in medicine and materials science.

C. Nonlinear Optical Spectroscopy

In earlier periods of AFOSR support, we commenced the development of femtosecond nonlinear spectroscopic techniques employing phase-sensitive detection for the simultaneous measurement of the real (nonlinear index of refraction phenomena) and imaginary (nonlinear absorption phenomena) components of various nonlinear susceptibilities. During the past grant period, we have extended capabilities to include frequency agility over the wavelength range 450 to 2500 nm. We have also extended capabilities to include multi-color laser experiments such as near-degenerate four wave mixing. Temporal resolution as short as 15 femtoseconds has been demonstrated. Development of instrumentation, theoretical analysis techniques, and applications of the technology is described in references 4,19,23,43,48,54,56,67.

1. Characterizing Electro-Optic Materials

Femtosecond techniques are useful for characterizing the electron dynamics of nonlinear optical materials (relevant to understanding bandwidth limitations of devices produced from materials) and for measuring properties such as two photon absorption (potentially relevant to understanding photodecomposition mechanisms of materials).⁵⁶ Our femtosecond instrumentation is routinely utilized to measure relevant properties of electro-optic chromophores.⁵⁶

2. Defining Two-Photon Absorption

Two-photon absorption is of interest in its own right for applications such as optical limiting (sensor protection), optical memory development, medical imaging, and photochemical initiation relevant to circuit fabrication by photoprocessing. Our instrumentation has been used as a resource by workers at both the Naval Research Laboratory^{4,19,23} and the Air Force Wright Laboratories.⁴³ Materials characterized include the fullerenes (C_{60} and C_{70}), the Air Force chromophore AF-50, and a variety of symmetrical analogs of electro-optic chromophores that exhibit very large two-photon cross-sections.

We have shown that our newly developed techniques are uniquely suited for quantitatively measuring two-photon absorption coefficients and lineshapes. Our techniques are unique in permitting extraction of two-photon resonances in the presence of one- and three-photon resonances, e.g., we have succeeded in characterizing all the H_g and A_g two-photon resonances (and observing the symmetry-defined splitting of the two-photon resonances of C_{70}) of the fullerenes lying within 8 eV of the HOMO.^{48,54} An invited talk on this latest work has been given at SPIE and will be published in the Proceedings. A manuscript is being prepared for submission to the *Physical Review Letters*.

D. Phase-Separating Block Copolymers

We have recently observed that a head-to-tail EO chromophore containing polymer block inserted into a phase-separating tetrablock copolymer can lead to finite macroscopic electro-optic activity when

interaction between "A" and "D" blocks is promoted by sequence specific hydrogen bonding and the "A" block has a carefully designed surface (substrate) binding affinity.^{38,39,71,77,81} This research is an attempt to systematically develop precisely nanostructured polymeric photonic materials.

E. Single Wall Carbon Nanotubes

1. Organic Actuators

We have already described opto-mechanical actuators based on polymers containing covalently coupled azobenzene moieties. We have, in collaboration with R. H. Baughman at Allied-Signal Corporation demonstrated electro-mechanical actuators based on single wall carbon nanotube paper.^{76,79,80} The actuation in these materials occurs by a new mechanism, namely, covalent bond expansion associated with electrochemical double-layer charge injection. Demonstrated actuators include unimorph and bimorph actuators operating in salt water, all-solid-state actuators, and micro-actuators. Demonstrated devices provide strains of over 2% for applied voltages of 1.5 volts or less. Initial prototype devices and the observation that the performance of actuators can be dramatically altered by modification of nanotube structure and the association (including covalent coupling) of individual nanotubes suggest that single wall carbon nanotube actuators may have significant advantages over any known device in terms of work-per-cycle and stress generation capabilities. Also, actuators based on single wall carbon nanotubes are capable of operating at extremely high temperatures as encountered for example in aerospace applications.

We have observed several maxima in graphs of strain versus frequency response (frequency of applied ac voltage). This suggests the possibility of several mechanisms of actuation with individual mechanisms dominating in specific frequency regimes.

2. Modification of Carbon Nanotubes

Our observation of a dramatic dependence of electro-mechanical actuator response on the structure of carbon nanotubes (different structures can be realized by different chemical and thermal treatments; for example, single and multi-wall nanotubes and individual as well as nanotube bundles can be produced by different treatment conditions). We have started a systematic characterization of structures by EM, Raman, and atomic imaging (STM/AFM/NSOM) techniques. We have started to explore the systematic modification of nanotubes to control nanostructural architecture.

Author of over 350 publications; AFOSR Publications Listed below)

1. L. R. Dalton, "Polymeric Electro-Optic Modulators," Chemistry & Industry, No. 13, 510-4 (1997).
2. A. K. Y. Jen, T. A. Chen, V. P. Rao, Y. Cai, Y. J. Liu, and L. R. Dalton, "High Performance Chromophores and Polymers for Electro-Optic Applications," Adv. Nonlinear Opt., **4**, 237-249 (1997).
3. L. R. Dalton, A. W. Harper, and B. H. Robinson, "The Role of London Forces in Defining Noncentrosymmetric Order of High Dipole Moment-High Hyperpolarizability Chromophores in Electrically Poled Polymeric Thin Films," Proc. Natl. Acad. Sci. USA, **94**, 4842-4847 (1997).
4. F. P. Strohkendl, L. R. Dalton, R. W. Hellwarth, H. W. Sarkas, and Z. H. Kafafi, "Phase-Mismatch in Degenerate Four-Wave-Mixing: The Complex Third-Order Susceptibility Tensor of C_{60} at 768 nm," J. Opt. Soc. Amer. B., **14**, 92-8 (1997).
5. L. R. Dalton, A. W. Harper, S. Sun, W. H. Steier, R. V. Mustacich, and A. K. Y. Jen, "Charge Transfer Interactions in Polymers and the Fabrication of High Frequency Electro-Optic Modulators," Macromol. Symp., **116**, 135-42 (1997).
6. D. Chen, H. R. Fetterman, A. Chen, W. H. Steier, L. R. Dalton, W. Wang, and Y. Shi, "High-Bandwidth Polymer Modulators," Proc. SPIE, **3006**, 314-17 (1997).
7. C. Koeppen, S. Yamada, G. Jiang, A. F. Garito, and L. R. Dalton, "Rare-Earth Organic-Complexes for Amplification in Polymer Optical Fibers and Wave-Guides," J. Opt. Soc. Amer. B., **14**, 155-62 (1997).
8. L. R. Dalton, A. W. Harper, J. Chen, S. Sun, S. Mao, S. Garner, A. Chen, and W. H. Steier, "The Role of Intermolecular Interactions in Fabricating Hardened Electro-Optic Materials," Proc. SPIE, **CR68**, 313-21 (1997).
9. A. Chen, V. Chuyanov, F. I. Marti-Carrera, S. Garner, W. H. Steier, J. Chen, S. Sun, and L. R. Dalton, "Integrated Polymer Waveguide Mode Size Transformer with a Vertical Taper for

- Improved Fiber Coupling," Optoelectronic Interconnects and Packaging IV, eds., R. P. Chen and P. S. Guilfoyle, Proc. SPIE, 3005, 65-76 (1997).
10. A. Chen, V. Chuyanov, F. I. Marti-Carrera, S. Garner, W. H. Steier, S. S. H. Mao, Y. Ra, L. R. Dalton, and Y. Shi, "Trimming of Polymer Waveguide Y-Junction by Rapid Photobleaching for Tuning the Power Splitting Ratio," IEEE Photonics Technology Letters, 9, 1499-501 (1997).
 11. S. Garner, V. Chuyanov, A. Chen, S. Kalluri, F. I. Marti-Carrera, W. H. Steier, and L. R. Dalton, "Three Dimensional Integrated Optics Using Polymers," in Organic Thin Films for Photonic Applications, Vol. 14, OSA Technical Digest Series (Optical Society of American, Washington DC, 1997), pp. 11-14.
 12. A. Chen, F. I. Marti-Carrera, V. Chuyanov, S. Garner, W. H. Steier, S. S. H. Mao, Y. Ra, L. R. Dalton, Y. Shi, "In-Situ Trimming of Polymer Optical Waveguides by Rapid Photobleaching for Tuning Device Specifications," in Organic Thin Films for Photonic Applications, Vol. 14, OSA Technical Digest Series (Optical Society of American, Washington DC, 1997), pp. 211-213.
 13. A. Chen, V. Chuyanov, S. Garner, W. H. Steier, L. R. Dalton, "Modified Attenuated Total Reflection for the Fast and Routine Electrooptic Measurements of Nonlinear Optical Polymer Thin Films," in Organic Thin Films for Photonic Applications, Vol. 14, OSA Technical Digest Series (Optical Society of American, Washington DC, 1997), pp. 158-159.
 14. A. Chen, V. Chuyanov, F. I. Marti-Carrera, S. Garner, W. H. Steier, J. Chen, S. Sun, S. S. H. Mao, Y. Ra, and L. R. Dalton, "Vertical Tapered Mode Size Transformer in Polymer Waveguides for Efficient Fiber Coupling," in Organic Thin Films for Photonic Applications, Vol. 14, OSA Technical Digest Series (Optical Society of American, Washington DC, 1997), pp. 8-10.
 15. A. Chen, S. Garner, A. Yacoubian, W. H. Steier, J. Chen, A. Harper, J. Zhu, M. He, S. Sun, F. Wang, Y. Ra, S. S. H. Mao, C. Zhang, L. R. Dalton, D. Chen, and H. R. Fetterman, "Characterization of Electro-Optic Polymers with High $\mu\beta$ Chromophores for Photonic Device Applications," in Organic Thin Films for Photonic Applications, Vol. 14, OSA Technical Digest Series (Optical Society of American, Washington DC, 1997), pp. 173-175.
 16. D. Chen, H. R. Fetterman, B. Tsap, A. Chen, W. H. Steier, L. R. Dalton, W. Wang, and Y. Shi, "Next Generation Ultra-High Frequency Integrated EO Modulators," in Organic Thin Films for Photonic Applications, Vol. 14, OSA Technical Digest Series (Optical Society of American, Washington DC, 1997), pp. 224-225.
 17. Y. Shi, W. Wang, J. H. Bechtel, W. H. Steier, L. R. Dalton, and H. R. Fetterman, "Integrated Electro-Optic Polymer Devices for Optical Communications," in Organic Thin Films for Photonic Applications, Vol. 14, OSA Technical Digest Series (Optical Society of American, Washington DC, 1997), pp. 229-231.
 18. A. W. Harper, M. He, F. Wang, J. Chen, J. Zhu, S. S. Sun, L. R. Dalton, A. Chen, S. M. Garner, A. Yacoubian, W. H. Steier, D. Chen, and H. R. Fetterman, "Recent Advances in the Translation of Large Microscopic Nonlinearities to Large Macroscopic Nonlinearities in Electro-Optic Polymer Films," in Organic Thin Films for Photonic Applications, Vol. 14, OSA Technical Digest Series (Optical Society of American, Washington DC, 1997), pp. 232-234.
 19. F. P. Strohkendl, T. J. Axenson, R. J. Larsen, L. R. Dalton, R. W. Hellwarth, and Z. H. Kafafi, "Observation of the Lowest Lying Electric-Dipole-Allowed Two-Photon Resonance in C_{60} ," J. Phys. Chem. B, 101, 8802-7 (1997).
 20. D. Chen, H. R. Fetterman, A. Chen, W. H. Steier, L. R. Dalton, W. Wang, and Y. Shi, "Demonstration of 110 GHz Electro-Optic Polymer Modulators," Appl. Phys. Lett., 70, 3335-3337 (1997).
 21. A. W. Harper, S. Sun, L. R. Dalton, S. M. Garner, A. Chen, S. Kalluri, W. H. Steier, and B. H. Robinson, "Translating Microscopic Optical Nonlinearity to Macroscopic Optical Nonlinearity: The Role of Chromophore-Chromophore Electrostatic Interactions," J. Opt. Soc. Amer. B, 15, 329-337 (1998); Opt. Soc. Amer. Tech. Digest, Solid State Lasers: Materials and Applications, 82-4 (1997).
 22. A. W. Harper and L. R. Dalton, "Identification of Critical Structure/Function Relationships in the Preparation of Polymer Thin Films for Electro-Optic Modulator Applications," Polym. Prepr.,

- 38, 500-1 (1997); also in Field Responsive Polymers: Electroresponsive, Photoresponsive, and Responsive Polymers in Chemistry and Biology, ACS Symposium Series 726 (I. M. Khan and J. Simpson, eds.) Amer. Chem. Soc., Washington, DC, 1998, Chapter 11.
23. F. P. Strohkendl, T. J. Axenson, R. J. Larson, L. R. Dalton, R. W. Hellwarth, and Z. H. Kafafi, "Two-Photon Absorption Spectra of C₆₉ and C₇₀ Between 0.7 and 1.7 μm ," Proc. SPIE, **3142**, 2-25 (1997).
24. A. Chen, V. Chuyanov, F. I. Marti-Carrera, S. Garner, W. H. Steier, and L. R. Dalton, "Fast Trimming of Electro-Optic Polymer Waveguide Y-branch by Post-Photobleaching for Tuning the Power Splitting Ratio," Proc. SPIE, **3147**, 268-74 (1997).
25. S. S. H. Mao, Y. Ra, L. Guo, C. Zhang, L. R. Dalton, A. Chen, S. Garner, and W. H. Steier, "Progress Towards Device-Quality Second-Order Nonlinear Optical Materials: 1. Influence of Composition and Processing Conditions on Nonlinearity, Temporal Stability and Optical Loss," Chemistry of Materials, **10**, 146-55 (1998).
26. L. R. Dalton and A. W. Harper, "Polymeric Electro-Optic Modulators: A Case Study in Supramolecular Chemistry and Integration of Disparate Materials," Polymer News, **23**, 114-120 (1998).
27. L. R. Dalton, "Polymers for Electro-Optic Modulator Waveguides," in Electrical and Optical Polymer Systems: Fundamentals, Methods, and Applications, eds. D. L. Wise, T. M. Cooper, J. D. Gresser, D. J. Trantolo, and G. E. Wnek, (World Scientific, Singapore, 1998), Chap. 18, pp. 609-661.
28. S. S. Sun, C. Zhang, Z. Yang, L. R. Dalton, S. M. Garner, A. Chen, and W. H. Steier, "Synthesis and Characterization of 1,3-Bis(dicyanomethylidene)Indane (BDMI) Based Nonlinear Optical Polymers," Polymer, **39**, 4977-81 (1998).
29. F. Wang, A. W. Harper, M. He, and L. R. Dalton, "Design and Synthesis of Perfluoroalkyldicyanovinyl-Based NLO Materials for Electro-Optic Applications," Polym. Prepr., **38**, 971-2 (1997); F. Wang, A. W. Harper, M. He, A. Ren, L. R. Dalton, S. M. Garner, A. Yacoubian, A. Chen, and W. H. Steier, "Design and Synthesis of a Perfluoroalkyldicyanovinyl-Based NLO Material for Electro-Optic Applications," Organic Thin Films, ACS Symposium Series 695 (C. W. Frank, ed.) Amer. Chem. Soc., Washington, DC, 1998, 252-7.
30. M. He, J. Zhu, A. W. Harper, S. S. Sun, L. R. Dalton, S. M. Garner, A. Chen, and W. H. Steier, "Progress Towards the Transition of Large Microscopic Nonlinearities to Large Macroscopic Nonlinearities for High- μB Materials," Organic Thin Films, ACS Symposium Series 695 (C. W. Frank, ed.) Amer. Chem. Soc., Washington, DC, 1998, 258-66.
31. Y. S. Ra, S. S. H. Mao, B. Wu, L. Guo, A. Chen, and W. H. Steier, "Thermoset Second-Order NLO Materials from a Trifunctionalized Chromophore," Organic Thin Films, ACS Symposium Series 695 (C. W. Frank, ed.) Amer. Chem. Soc., Washington, DC, 1998, 288-94.
32. J. Chen, J. Zhu, G. Todorova, M. He, L. R. Dalton, S. Garner, A. Chen, W. H. Steier, "High E-O Coefficient Polymers Based on a Chromophore Containing Isophorone Moiety for Second Order Nonlinear Optics," Materials Research Society Symposium Proceedings, **Vol. 488, Electrical, Optical and Magnetic Properties of Organic Solid State Materials** (Materials Research Society, Pittsburgh, 1998) p. 151-6.
33. A. W. Harper, J. Zhu, M. He, L. R. Dalton, S. M. Garner, and W. H. Steier, "Characterization and Circumventing Electrostatic Intermolecular Interactions in Highly Electro-Optic Polymers," Materials Research Society Symposium Proceedings, **Vol. 488, Electrical, Optical and Magnetic Properties of Organic Solid State Materials** (Materials Research Society, Pittsburgh, 1998) p. 199-209.
34. A. K.-Y. Jen, Q. Yang, S. R. Marder, L. R. Dalton, C. F. Shu, "Recent Progress of Electro-Optic Polymers for Device Applications," Materials Research Society Symposium Proceedings, **Vol. 488, Electrical, Optical and Magnetic Properties of Organic Solid State Materials** (Materials Research Society, Pittsburgh, 1998) p. 193-7.
35. S. Garner, V. Chuyanov, A. Chen, S. S. Lee, W. H. Steier, and L. R. Dalton, "Integrated Optic, Vertical Polarization Splitters Using Polymers," Proc. SPIE, **3278**, 259-64 (1998).

36. J. R. Reynolds, A. K. Y. Jen, L. R. Dalton, M. F. Rubner, and L. Y. Chiang, Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials IV. (Materials Research Society, Pittsburgh, 1998).
37. A. Chen, V. Chuyanov, H. Zhang, S. Garner, W. H. Steier, J. Chen, J. Zhu, M. He, S. S. H. Mao, and L. R. Dalton, "Demonstration of the Full Potential of Second Order Nonlinear Optic Polymers for Electrooptic Modulation Using a High $\mu\beta$ Chromophore and a Constant Bias Field," Optics Lett., **23**, 478-80 (1998).
38. J. Pan, P. Warner, L. R. Dalton, and T. E. Hogen-Esch, "Block Copolymerization Towards Asymmetric Self-Assembly," Polym. Prepr., **39**, 576-7 (1998); full manuscript submitted to Macromolecules.
39. J. Pan, D. Huang, M. Chen, M. He, W. Weber, L. R. Dalton, and T. E. Hogen-Esch, "Synthesis of Block Copolymers Containing Main Chain NLO Segments," Polym. Prepr., **39**, 578-80 (1998); full manuscript submitted to Macromolecules.
40. L. R. Dalton, "Polymers for Electro-Optic Waveguides," Plast. Eng., **45**, 609-61 (1998).
41. A. Chen, V. Chuyanov, H. Zhang, S. Garner, S. S. Lee, W. H. Steier, J. Chen, F. Wang, J. Zhu, M. He, Y. Ra, S. S. H. Mao, A. W. Harper, L. R. Dalton, and H. R. Fetterman, "Low V_π High Thermal Stability Electro Optic Polymer Waveguide Modulators Using the Full Potential of High $\mu\beta$ Chromophores with a DC Bias Voltage," Proc. SPIE, **3281**, 94-105 (1998).
42. S. M. Garner, S. S. Lee, V. Chuyanov, A. Yacoubian, A. Chen, W. H. Steier, J. Zhu, J. Chen, F. Wang, A. S. Ren, and L. R. Dalton, "Vertically Integrated Polymer Waveguide Device Minimizing Insertion Loss and V_π ," Proc. SPIE, **3491**, 421-6 (1998).
43. P. A. Fleitz, M. C. Brant, R. L. Sutherland, F. P. Strohkendl, R. J. Larsen, and L. R. Dalton, "Nonlinear Measurements on AF-50," Proc. SPIE, **3472**, 91-7 (1998).
44. S. S. Lee, S. Garner, A. Chen, V. Chuyanov, W. H. Steier, L. Guo, L. R. Dalton, and S. Y. Shin, "Patterned Birefringence by Photo-Induced Depoling in Electro-Optic Polymers and Its Application to a Waveguide Polarization Splitter," Appl. Phys. Lett., **73**, 3052-4 (1998).
45. L. R. Dalton, "Nonlinear Optical Materials," in Kirk-Othmer Concise Encyclopedia of Chemical Technology, John Wiley & Sons, New York, 1999, p. 1377.
46. D. Chen, D. Bhattacharya, A. Udupa, B. Tsap, H. R. Fetterman, A. Chen, S. S. Lee, J. Chen, W. H. Steier, and L. R. Dalton, "High-Frequency Polymer Modulators with Integrated Finline Transitions and Low V_π ," IEEE Photonics Technology Letters, **11**, 54-56 (1999).
47. L. R. Dalton, A. W. Harper, A. Ren, F. Wang, G. Todorova, J. Chen, C. Zhang, and M. Lee, "Polymeric Electro-Optic Modulators: From Chromophore Design to Integration with Semiconductor VLSI Electronics and Silica Fiber Optics," Ind. Eng. Chem. Res., **38**, 8-33 (1999).
48. K. A. Drenser, R. J. Larsen, F. P. Strohkendl, and L. R. Dalton, "Femtosecond, Frequency-Agile, Phase Sensitive Detected, Multi-Wave-Mixing Nonlinear Optical Spectroscopy Applied to π -Electron Photonic Materials," J. Phys. Chem., **103**, 2290-2301 (1999).
49. S. T. Wu, C. S. Hsu, K. F. Shyu, Y. Y. Chuang, H. B. Cheng, Z. Chai, G. Day, L. Guo and L. R. Dalton, "High Birefringence Bis-Tolane Liquid Crystals for Display Applications," SID Tech. Digest, **30**, 706-9 (1999).
50. A. K. Y. Jen, Y. Liu, L. Zheng, S. Liu, K. J. Drost, Y. Zhang, and L. R. Dalton, "Synthesis and Characterization of Highly Efficient, Chemically and Thermally Stable Chromophores with Chromone-Containing Electron Acceptors for NLO Applications," Adv. Mater., **11**, 452-5 (1999).
51. S. M. Garner, V. Chuyanov, S.-S. Lee, A. Chen, W. H. Steier, and L. R. Dalton, "Vertically Integrated Waveguide Polarization Splitters Using Polymers," IEEE Photonics Technology Letters, **11**, 842-4 (1999).
52. A. K. Y. Jen, H. Ma, X. Wu, J. Wu, S. Liu, S. R. Marder, L. R. Dalton, and C. F. Shu, "Recent Development of Highly Efficient Chromophores and Polymers for Electro-optic Device Applications," Proc. SPIE, **3623**, 112-9 (1999).
53. S. M. Garner, S.-S. Lee, V. Chuyanov, A. Chen, A. Yacoubian, W. H. Steier, and L. R. Dalton, "Three Dimensional Integrated Optics Using Polymers," IEEE Journal of Selected Topics in Quantum Electronics, **35**, 1146-55 (1999).

54. L. R. Dalton, F. P. Strohkendl, and, R. J. Larsen, "Measurement of Two-Photon Absorption Coefficients Employing Femtosecond, Phase-Mismatched DFWM and n-DFWM Spectroscopy," Nonlin. Opt., **21**, 245-61 (1999).
55. L. R. Dalton, W. H. Steier, B. H. Robinson, C. Zhang, A. Ren, S. Garner, A. Chen, T. Londergan, L. Irwin, B. Carlson, L. Fifield, G. Phelan, C. Kincaid, J. Amend, and A. Jen, "From Molecules to Opto-Chips: Organic Electro-Optic Materials," J. Chem. Mater., **9**, 1905-21 (1999).
56. B. H. Robinson, L. R. Dalton, A. W. Harper, A. Ren, F. Wang, C. Zhang, G. Todorova, M. Lee, R. Anisfeld, S. M. Garner, A. Chen, W. H. Steier, S. Houbrecht, A. Persoons, I. Ledoux, J. Zyss, and A. K. Y. Jen, "The Molecular and Supramolecular Engineering of Polymeric Electro-Optic Materials," Chem. Phys., **245**, 35-50 (1999).
57. W. H. Steier, A. Chen, S.-S. Lee, S. Garner, H. Zhang, V. Chuyanov, L. R. Dalton, F. Wang, A. S. Ren, C. Zhang, G. Todorova, A. W. Harper, H. R. Fetterman, D. Chen, A. Udupa, D. Bhattacharya, and B. Tsap, "Polymer Electro-Optic Devices for Integrated Optics," Chem. Phys., **245**, 487-506 (1999).
58. F. P. Strohkendl, T. J. Axenson, R. J. Larsen, L. R. Dalton, R. W. Hellwarth, and Z. H. Kafafi, "Nonlinear Optical Spectra of C₇₀," Chem. Phys., **245**, 285-300 (1999).

AFOSR Manuscripts Submitted for Publication

59. H. Ma, A. K. Y. Jen, J. Wu, X. Wu, S. Liu, C. F. Shu, L. R. Dalton, S. Thayumanavan, and S. R. Marder, "A Generic Approach of Functionalizing Aromatic Polyquinolines for Electro-Optic Devices," submitted to Chemistry-A European Journal.
60. L. R. Dalton, A. Ren, M. S. Lee, A. W. Harper, B. H. Robinson, S. M. Garner, S. S. Lee, and W. H. Steier, "Development of Opto-Chips Based on Polymeric Electro-Optic Modulators," Adv. Mater., invited article, in press.
61. S. S. H. Mao, Y. S. Ra, M. He, J. Zhu, C. Zhang, L. R. Dalton, S. Garner, and W. H. Steier, "Progress Toward Device-Quality Second-Order NLO Materials. 2. Enhancement of Electric Poling Efficiency and Temporal Stability by Modification of Isoxazolone Based High $\mu\beta$ Chromophores," Chemistry of Materials, in press.
62. Fang Wang, Aaron W. Harper, Michael S. Lee, Larry R. Dalton, Hua Zhang, Antao Chen, William H. Steier, and Seth R. Marder, "Progress Toward Device-Quality Second-Order NLO Materials. 3. Electro-Optic Activity of Polymers Containing *E,E,E*-4-(*N,N* dialkyl amino)-phenylpentadienylidene 3-phenyl-5-isoxazolone Chromophores," Chem. Mater., in press.
63. A. Ren and L. R. Dalton, "Electroactive Polymers Including Nonlinear Optical Polymers," Current Opinion in Colloid & Interface Science, invited article, in press.
64. S. M. Garner, S.-S. Lee, V. Chuyanov, A. Yacoubian, A. Chen, W. H. Steier, F. Wang, A. S. Ren, M. He, and L. R. Dalton, "Vertically Integrated Polymer Waveguide Modulator Utilizing a Hybrid Design," IEEE Photonics Technology Letters, in press.
65. S. S. H. Mao, Y. S. Ra, L. Guo, C. Zhang, L. R. Dalton, A. Chen, and W. H. Steier, "Progress Toward DeviceQuality Second-Order NLO Materials. 4. Deteriorative Effect of Chromophore Aggregation on Optical Loss," Chemistry of Materials, submitted.
66. S. S. Lee, S. Garner, V. Chuyanov, H. Zhang, W. H. Steier, F. Wang, L. R. Dalton, A. Udupa, and H. R. Fetterman, "Optical Intensity Modulator Using a Novel Thermal Corsslinkable Electrooptic Polymer," Appl. Phys., submitted.
67. R. J. Larsen, F. P. Strohkendl, and L. R. Dalton, "Degenerate Four-Wave Mixing and Two-Photon Absorption Spectra of AF50 Between 0.54 and 1.2 μm ," J. Chem. Phys., submitted.
68. C. Zhang, A. S. Ren, F. Wang, J. Zhu, L. R. Dalton, J. N. Woodford, and C. H. Wang, "Synthesis and Characterization of Thermally Stable Ring-Locked Phenyltriene Bridged Second-Order Nonlinear Optical Chromophores," Chem. Mater., in press.
69. Liakatas, C. Cai, M. Bosch, M. Jager, Ch. Bosshard, P. Gunter, C. Zhang, and L. R. Dalton, "Intermolecular Interactions of Highly Nonlinear Optical Molecules for Electro-Optic Polymer Applications," Organic Thin Films for Photonic Applications, in press.
70. A. H. Udupa, H. Erlig, Y. Chang, D. H. Chang, D. Bhattacharya, B. Tsap, H. R. Fetterman, S. S. Lee, H. Zhang, W. H. Steier, C. Zhang, and L. R. Dalton, "Demonstration of a Photonicallly Controlled RF Phase Shifter," IEEE Photonics Technology Letters, in press.

71. T. Londergan and L. R. Dalton, "Control of Optical Properties Using Various Nanostructured Materials: Dendrimers, Phase-Separating Block Copolymers, and Polymer Microspheres," in Frontiers of Polymers and Advanced Materials, ed. P. N. Prasad et al., Gordon and Breach, New York, 1999.
72. I. Liakatas, C. Cai, M. Bosch, M. Jager, Ch. Bosshard, P. Gunter, C. Zhang, and L. R. Dalton, "Importance of Intermolecular Interactions on the Nonlinear Optical Properties of Poled Polymers," Appl. Phys. Lett., in press.
73. Y. Shi, W. Lin, D. J. Olson, J. H. Bechtel, H. Zhang, W. H. Steier, C. Zhang, and L. R. Dalton, "Electrooptic Polymer Modulators with 0.1 V Halfway Voltage," Appl. Phys. Lett., in press.
74. Y. Shi, W. Lin, D. J. Olson, J. H. Bechtel, H. Zhang, W. H. Steier, C. Zhang, "Realization of Sub 1-V V_{π} Electro-Optic Modulators," Science, submitted.
75. L. R. Dalton, "Polymeric Electro-Optic Materials: Optimization of Electro-Optic Activity, Minimization of Optical Loss, and Fine-Tuning of Device Performance," Opt. Eng., in press.
76. R. H. Baughman, Changxing Cui, Anvar A. Zakhidov, and William Kuhn, Joseph N. Barisci, Geoff M. Spinks, Gordon G. Wallace, Alberto Mazzoldi, Danilo De Rossi, Andrew Rinzler, Siegmund Roth, Leonard Fifeild, Larry Dalton, "Carbon Nanotube Electromechanical Macroactuators and Microactuators," Proc. SPIE (in press).
77. D. Huang, C. Zhang, L. R. Dalton, and W. P. Weber, "Synthesis and Characterization of Main-Chain NLO Oligomers and Polymers Which Contain 4-Dialkylamino-4'-(alkylsulfonyl) azobenzene Chromophores," J. Polym. Sci., A: Polym. Chem., submitted.
78. B. H. Robinson and L. R. Dalton, "Equilibrium and Non-Equilibrium Statistical Mechanical Treatment of Intermolecular Electrostatic Interactions," J. Phys. Chem., in press.
79. R. H. Baughman, Changxing Cui, Anvar A. Zakhidov, and William Kuhn, Joseph N. Barisci, Geoff M. Spinks, Gordon G. Wallace, Alberto Mazzoldi, Danilo De Rossi, Andrew Rinzler, Siegmund Roth, Leonard Fifeild, Larry Dalton, "Electrochemically Controlled Creep and Shape Memory Effects in Carbon Nanotube Paper," Science, submitted.
80. R. H. Baughman, Changxing Cui, Anvar A. Zakhidov, and William Kuhn, Joseph N. Barisci, Geoff M. Spinks, Gordon G. Wallace, Alberto Mazzoldi, Danilo De Rossi, Andrew Rinzler, Siegmund Roth, Leonard Fifeild, Larry Dalton, "Solid-State Electrolyte/Nanotube Complexes," Science, submitted.
81. D. Huang, C. Zhang, L. R. Dalton, and W. P. Weber, "Sequential Synthesis of Main-Chain NLO Oligomers which Contain 4-Dialkylamino-4'-(alkylsulfonyl)azobenzene Chromophores," Designed Monomers and Polymers, submitted.

REFERENCES & FOOTNOTES

82. F. London, Trans. Faraday Soc., **33**, 8-26 (1937).
83. A. Piekara, Proc. Roy. Soc. A, **172**, 360-83 (1939).
84. A. Ren, Ph.D. Thesis, University of Southern California, Los Angeles, 1999. A. Ren and L. R. Dalton, unpublished results.
85. L. R. Dalton, A. W. Harper, R. Goshn, W. H. Steier, M. Ziari, H. Fetterman, Y. Shi, R. V. Mustacich, A. K. Y. Jen, and K. J. Shea, "Synthesis and Processing of Improved Organic Second-Order Nonlinear Optical Materials for Applications in Photonics," Chem. Mater., **7**, 1060-81 (1995).
86. Y. Shi, W. H. Steier, L. Yu, M. Chen, and L. R. Dalton, "Large Photoinduced Birefringence in an Optically Nonlinear Polyester Polymer," Appl. Phys. Lett., **59**, 2935-7 (1991); L. R. Dalton, L. S. Sapochak, M. Chen, and L. P. Yu, "Ultrastructure Concepts of Optical Integrated Microcircuits and Polymeric Materials," in Molecular Electronics and Molecular Electronic Devices, Vol. 2, ed., K. Sienicki (CRC Press, Boca Raton, 1993) pp. 125-208 and references contained therein.
87. T. Forster, Ann. Physik, **2**, 55 (1948); T. Forster, Z. Naturforsch., **44**, 319 (1949).
88. S. L. Gilat, A. Adronov, J. M. J. Frechet, Angew. Chem. Int. Ed. Engl., **38**, 1422-7 (1999); S. Hecht and J. M. J. Frechet, J. Am. Chem. Soc., **121**, 4084-5 (1999); M. Kawa and J. M. J. Frechet, Thin Solid Films, **331**, 259-63 (1998); P. R. L. Malenfant, L. Groenendaal, and J. M. J. Frechet, J. Am. Chem. Soc., **120**, 10990-1 (1998); S. C. Koene, K. A. Kileen, M. E. Thompson, A. Freeman, and J. M. J. Frechet, Polym. Mat. Sci. Eng., **80**, 238-9 (1999).

PERSONNEL SUPPORTED

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Ms. Jinghong Chen, graduate research assistant
Mr. Aaron Haprer, graduate research assistant

Program Statistics

- 65. Number of PI and Co-PI involved in the research project: 1
- 66. Number of Post Doctoral Fellows supported: 3
- 67. Number of Graduate Students supported: 7
- 68. Number of other researchers supported: 0
- 69. Number of publications by PI: 109
- 70. Number of publications that acknowledge AFOSR support: 81
- 71. Awards and Honors received by PI: 9

Transitions:

- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. Todd McIntyre, Microvision, 425-415-6616, d. For telecommunication and display applications
- b. Dalton, Univ. of Washington, b. Electro-optic materials, c. Martin A. Kits van Heyningen, KVH Industries, 401-847-3327, d. In-line fiber telecommunication applications
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. Araz Yacoubian and James H. Bechtel, IPITEK, 760-438-8362, d. Prototype push-pull modulator fabrication
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. Harold Fetterman and Joseph Michael, Pacific Wave, 310-229-009, d. Prototype device fabrication
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. Susan Ermer, Lockheed Martin, 650-424-3131, d. Prototype device evaluation for various defense applications
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. John Zhang, Lumera Corporation, 425-415-6757, d. Telecommunications and data processing applications
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. Jeffery Make and Ray Chen, Radiant Research, 512-471-7035, d. Prototype device fabrication and evaluation
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. William Owens, Teledesic, 425-602-0000, d. Telecommunications (phased array radar) applications
- a. Dalton, Univ. of Washington, b. Sensor materials, c. Jonathan Saint Clair, Boeing, 253-773-8987, d. Sensor paints
- a. Dalton, Univ. of Washington, b. Single wall carbon nanotube actuators, c. Ray Baughman, Honeywell (Allied Signal), d. Actuators for various applications
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. Paul Hale and Eric Amis, NIST, 301-975-6681, d. Evaluation of performance characteristics
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. James Grote, AFRL-Wright-

Patterson, d. Prototype device fabrication and evaluation

- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. David Weymouth, JDS Uniphase, 613-727-1304, d. Optical network applications
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. Geoff Lindsay and Paul Ashley, Navy China Lake and Army Redstone Arsenal, d. Optical gyroscopes
- a. Dalton, Univ. of Washington, b. Light harvesting solar cell coatings, c. Kitt C. Reinhardt, AFRL/VSSV, Kirtland, NM, d. Improved efficient solar cells
- a. Dalton, Univ. of Washington, b. Electro-optic modulators, c. Shane Stutz, Naval Research Laboratory, 202-404-1514, d. Evaluation of prototype modulators
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. Andre Knossen, Univ. of California at Davis, d. Prototype modulator development
- a. Dalton, Univ. of Washington, b. Electro-optic materials, c. Jeff Woodford and C. H. Wang, Univ. of Nebraska, d. Materials evaluation

List of Awards

- 2000 Distinguished Alumni Award of Michigan State University
- 1996 Richard C. Tolman Award of the Southern California Section, American Chemical Society
- Paul C. Cross Lectureship, University of Washington, Seattle, WA (1996)
- NASA Lecturer, 54th Frontiers in Chemistry Lecture Series (1995), Case Western Reserve University
- The 1990 Univ. of Southern California Associates Award for Creativity in Research and Scholarship
- 1986 Burlington Northern Foundation Faculty Achievement Award
- NIH Research Career Development Awards (Two Awards; 75-81)
- Camille and Henry Dreyfus Teacher-Scholar Award (75-77)
- Alfred P. Sloan Fellowship (74-77)